Review Portland Food Web Modeling Effort

Focus of Review:

1) Review model parameterization to identify any inappropriate parameter definitions and recommend any necessary changes.

After looking over the model parameterization/input data, nothing appears to be way out of line or inappropriate

2) Review model modifications: The LWG made some modifications to the Gobas model as received from Bruce Hope to "make it work better". An assessment of the utility and validity of these modifications should be performed.

The Portland model uses the equations of Arnot & Gobas. I'm bit opposed to modification of the internal parameters of the Arnot & Gobas model. The suggestion that the Portland Harbor data is of better quality than those used by Arnot & Gobas to build and validate their model seems to be a bit of an over reach. I suspect that given the complexities of the site that the data are not of higher quality.

The modifications are the optimization of 21 internal parameters. I have the feeling that because they could do this easily, they did it. Not because something was wrong with the model parameterization by Arnot & Gobas. Without doing a whole bunch of work, I can not tell you if this was appropriate.

3) The LWG used surface weighted average concentrations (SWACs) to develop average sediment concentrations. This is the same issue we recently addressed in the review of the Duwamish River FWM, so we would like comment on the appropriateness of this approach.

The use of a site wide SWAC value assumes that the organism uses the entire site. Further, the SWAC was computed assuming equal chemical bioavailability across the site, and this is not true based upon the data from the lab worm and clam testing data, and the clam field data. Because model is constructed using a single water and sediment input concentrations, some type of averaging will be required. One possibility might be to drive the food web model with residues in the worm and clam data rather than the residues in the sediment.

4) Provide recommendations on the predictive ability of the food web model - i.e. are the model predictions sufficiently accurate to meet the two purposes of the FWM described above? We currently are not convinced that the model predictions are sufficiently accurate for all chemicals and species for which predictions are required. For example, some of the TEQ in tissue predictions are no better than between 5x and 10x of the empirical data, which we do not believe allows site managers to have confidence in the FWM output for those parameters.

I suspect (but don't know) that issues with the TEQ predictions are influenced by data quality issues. Given how the model works for other non-polar organic

chemicals, there is no reason why the model should not have similar predictive ability for the TEQ chemicals.

5) Review the suite of chemicals modeled, the species modeled, and comment on the agreed upon lists. A concern currently held by both Burt Shephard and Bruce Hope is that the current iteration of the FWM may be overspecified. If this is the case, we would like suggestions regarding ways to address this issue.

Because of the nature of food web models, there are 70 input parameters for the model. Further, the modelers chose to optimize 21 internal parameters that results in a total of 91 parameters being optimized. Given the limited number of average values used in the Monte Carlo process, I believe the model is highly calibrated to the field data used in the calibration process and what ever deficiencies exist in these data are captured in the calibration process. Checking the model with new data will help in understanding the accuracy of the predictions from Portland Harbor model.

In terms of simplifying the model, the only thing that can be easily done is to cut back in the Monte Carlo analysis to the 70 input parameters, and use the Arnot & Gobas parameterization for the 21 internal parameters. I don't know if this would really improve predictive ability.

I have no real comments on the chemical and species modeled. Those items are not a science question but rather site decision.

On a personal basis, I prefer modeling chemical individually, and then, combining them after making the predictions. This avoids the messy averaging done prior to the make the food web predictions. This would also eliminate the problems with differing compositions of the mixture across the site. The predictiveness of the model might improve using this approach for mixtures.

What is the Arnot & Gobas model?

If one downloads the Arnot & Gobas food web model (AQUAWEBv1.2_BIOv1.2.xls), the model inputs are the following parameters:

Site Specific Environmental Parameters
- Mean Water Temperature
- Dissolved Organic Carbon Content (OCwat)
- Particulate Organic Carbon Content (POC)
- Concentration of Suspended Solids (Vss)
- Sediment Organic Carbon Content (OCsed)
- Mean Water Column Dissolved Oxygen Saturation (SAT) (default of 90%)
  - Or Dissolved Oxygen Content

Site Specific Biological Parameters
- Species Name
- Species Wet Weight (kg)
- Species Whole Body Lipid Content (%)
- Species Moisture Content (%)
- Species NLOM Content (%) (default of 20%)
- Fraction of Pore Water Ventilated (Pw)
- Feeding Preferences

Site Specific Chemical Parameters
- Chemcal Name
- log Kow (unitless)
- Total Water Concentration (ng/L)
- Sediment Concentration (ng/g dry weight)
- Metabolic Transformation Rate Constant (kM)

With these input parameters, residues are predicted for each species in the food web. No other parameters are adjusted or changed in calculating the results.

In the analysis presented in Appendix E, in addition to the input parameters above, a whole series of parameters, internal to the Arnot & Gobas model, are adjusted by using the Monte Carlo analysis. These additional internal parameters are:
- dietary absorption efficiencies for lipid (eL) and NLOM (eN)
- phytoplankton uptake constants A and B
- NLOM proportionality constant BETA

Note, the dietary absorption efficiencies were optimized for each species.

The modeling effort performed begs the question, "Was the Arnot & Gobas model used?". Well, the equations and constructs of Arnot & Gobas were used, however, their parameterization was not used. Examination of Tables 3-5, 3-6, and 3-7 reveals that the calibrated values for environmental, general biological, and species-specific parameters are largely unchanged from those used by Arnot & Gobas except for:
- crayfish dietary absorption efficiency of lipid and NLOM
- clams dietary absorption efficiency of lipid

- phytoplankton uptake constants A and B

From Tables 3-5, 3-6, 3-7 and 3-8, there are

4 – environmental parameters
3 – general biological parameters of which 3 are internal parameters
52 – species-specific biological parameters of which 18 are internal parameters
32 – species-specific dietary parameters

resulting in

91 – total parameters (of which 21 are Arnot & Gobas internal parameters)

that are optimized in the Monto Carlo procedure. There are 10 different species in the food web and only 5 of the species (clams, carp, crayfish, sculpin, and smallmouth bass) have values for PCBs 17, 170 and 206. These five values are used in calibrating the model, i.e., providing the "calibrated" values reported in Tables 3-5, 3-6, 3-7 and 3-8. What I don't understand is how the "calibrated" values for the largescale sucker and northern pikeminnow are derived using PCBs 17, 170, and 206 when these species have no data for these congeners (see Appendix E2, Table 1). For the lower trophic levels, i.e., phytoplankton, zooplankton, and benthic invertebrates, their calibrated values can be found based upon the their predator residues.

From a modeling perspective, the model codes are those of Arnot & Gobas and the only differences between the Portland Harbor model and the Arnot & Gobas model are the values for the 21 internal parameters discussed above. I'm struggling to say that optimizing these 21 parameters in this modeling effort is good or wise effort. Why? Arnot & Gobas went to great lengths in assembling data that were of high quality across a number of food webs and these data have coverage of all species in these food webs. Subsequently, they used these data to validate their model. The effort here assumes that their data are of higher quality/better than that used by Arnot & Gobas. I'm not so sure that the Portland Harbor data are of higher quality given the complexities of the site, and the bioavailability issue discussed below. Further, why did the modelers choose to optimize these specific 21 internal parameter and not all of the parameters in the model, e.g., equations for growth, respiration, etc.? In part, by opening this can of worms, the modelers are suggesting that they know more than Arnot & Gobas, and that by optimizing these 21 internal parameters, the Portland Harbor model will have better predictive power than the Arnot & Gobas model. Mathematically with the 5 average values, the Portland Harbor model does provide a good fit, i.e., SPAFs are small, but I suspect that the Arnot & Gobas model (with Arnot & Gobas parameterization) would provide similar fits.

Regardless, nothing appears to have been done improperly on the execution of the Monte Carlo technique. The SPAFs, and sensitivity and uncertainty analyses demonstrates that Portland Harbor model does fit the field data from the site reasonably well. These analyses don't speak or address the issue of the quality of field data. The quality of the predictions from the Portland Harbor model are predicated upon the quality of the field data and if quality of the data is low, the model will provide poor predictions, in essence, garbage in – garbage out. To address the issue of the quality of the field data, additional data sets from time periods totally independent of the calibration data are required. With

these data, predictions based upon the conditions (concentrations of chemical in sediment and water) can be made and then, compared to independent data. These would provide a much better indication of the predictive power of the Portland Harbor model.

Given the number of parameters being optimized with the Monte Carlo technique and the relatively limited amounts of the field data, the model seems over parameterized. Without the 21 internal parameters, there are 70 input values being optimized with the Monte Carlo technique. Of the 70 inputs values, 32 are diet, 9 are weight, 10 are lipid content, and 10 are moisture content, and all of these values are required input values for the model. Unfortunately, this is the nature of food web model.

The harbor wide calibrated Portland Harbor food web model was executed at smaller scales and on laboratory test data. In general, the fits (SPAFs) were poorer, and these results were not surprising given that the model is highly calibrated to harbor wide average values.

Mixtures with the Food Web Model

The calibrated food web model was used to make predictions for chemical groups, e.g., total DDTs, total PCBs, PCB TEQs (birds), PCB TEQ (mammals), Dioxin TEQ (birds), and Dioxin TEQ (mammals). Predictions for mixtures are predicated upon have the correct weighted average K_{ow} of the mixture. If the composition of the mixture is not the same across the harbor, predictions will be inaccurate. For example, the SWAC for the surface sediment averages the total from each surface sample and if the compositions vary widely among surface samples, selecting an appropriate K_{ow} will be difficult.

BSAF Regression Equations

The plots of BSAF vs concentrations of the chemical in the sediment on an organic carbon basis reveals a trend of decreasing BSAF with increase concentration in the sediment. For the laboratory derived BSAFs for worms and clams, the BSAFs are generally below 10 for low concentrations in sediment. Field clams BSAF have the same behavior.

The regressions appear to have been properly done. However, the equations in BSAF_eqns_shellfish_052907.xls don't line up exactly with data in FieldClams_BSAFs.xls. I'm probably missing something. Some of the regressions don't have much predictive power, e.g., aldrin has a r^2 of 16% for shellfish.

Chemical Bioavailability

What is bothersome is the fact that chemical bioavailability changes with increasing concentration of the chemical in the sediment on an organic carbon basis, i.e., BSAFs decline with increasing concentration in the sediment. I don't believe that the observed trend is a sampling fluke because the laboratory testing data confirms the field observation. There are a number reasons why chemical bioavailability could be changing. First, the presence of black carbon, and second, the presence of oil/grease like phase. Both of these phases have much higher sorptive capacity for the organic contaminants of interest, and their presence in a harbor would not be unexpected.

Because the spreadsheets of data don't contain the organic carbon content of the sediments, one can not determine if the BSAFs decrease with increasing organic carbon content. If so, this observation would point one in the direction of having a black carbon and/or oil/grease phases present.

The observation of declining bioavailability with increasing concentrations in the sediment has implications. Presently, I'm not totally sure of what these implications are, i.e., sediment PRGs being too small or too large.

Quality of Field Data

The development of BSAFs and the Portland Harbor food web are dependent upon the quality of the field data. The PCDD and PCDF data seem out of line with the PCBs in their bioaccumulation behavior. This is comment is based upon Round 1 data and some work I have done with BSAFs calculated using site data. There also are samples that seem to be outliers. For example, sediment sample "LWG0107R006SDS015C00" has usually high PCDF values relative to other samples and to its own PCDD levels; i.e., 2,3,7,8-TCDF is 14,000 pg/g while 2,3,7,8-TCDD is 5.4 pg/g, and other samples are 1,000-10,000 fold lower for 2,3,7,8-TCDF.

Summary Comments

The Arnot & Gobas model has been used with modification to 21 internal parameters. The Portland Harbor model is high calibrated with field data from the site. The calculations with the model appear to have been done correctly. The regression equations for predicting residues in tissue based upon concentration of chemical in the sediment were done correctly. There tends to be a lot scatter in the data, and I wonder if the regressions have any predictive ability. Many of the predictions were done for mixtures, and if the composition of the mixture changes across the harbor, then predictions will be inaccurate and have high uncertainty. (This issue is not addressed in Appendix E.) This influences both food web predictions and BSAF calculations. The inverse dependence of BSAFs upon concentration of the chemical in sediment on an organic carbon basis indicates that bioavailability changes with increasing concentration in the sediment. This issue isn't addressed in the SWAC calculation while the field measured BSAFs incorporate these influences.